

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01L 21/302	A1	(11) International Publication Number: WO 98/32163 (43) International Publication Date: 23 July 1998 (23.07.98)
(21) International Application Number: PCT/US98/01296 (22) International Filing Date: 22 January 1998 (22.01.98) (30) Priority Data: 60/035,307 22 January 1997 (22.01.97) US (71) Applicant: CALIFORNIA INSTITUTE OF TECHNOLOGY [US/US]; 1200 East California Boulevard, Pasadena, CA 91125 (US). (72) Inventors: TAI, Yu-Chong; Pasadena, CA (US). WANG, Xuan-Oi; Pasadena, CA (US). (74) Agent: HARRIS, Scott, C.; Fish & Richardson P.C., Suite 1400, 4225 Executive Square, La Jolla, CA 92037 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: GAS PHASE SILICON ETCHING WITH BROMINE TRIFLUORIDE (57) Abstract An apparatus and method for gas-phase bromine trifluoride (BrF ₃) silicon isotropic room temperature etching system for both bulk and surface micromachining. The gas-phase BrF ₃ can be applied in a pulse mode and in a continuous flow mode. The etching rate in pulse mode is dependent on gas concentration, reaction pressure, pulse duration, pattern opening area and effective surface area.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

Gas Phase Silicon Etching with Bromine TrifluorideField of the Invention

This disclosure relates to pulsed gas-phase
5 silicon etching in micromachining processes. More
specifically, etching using BrF_3 is described.

Background

Etching is used to form features during silicon
micromachining in micro-electromechanical systems ("MEMS").
10 The success of etching processes are characterized by the
etch rate in dimensions of thickness per unit time. The
etch rate has dimensions of thickness per unit time. A
high etch rate is generally desired. However, too high
an etch rate may render a process difficult to control.
15 Common desired etch rates are in units of hundreds or
thousands of angstroms per minute. Selectivity is the
ratio of the etch rates of silicon referenced to the etch
rate of the mask film being patterned on top of silicon.
A particular process may be quoted as having a
20 selectivity of 300 to 1, polysilicon over oxide. This
means that polysilicon etches 300 times faster than
oxide. Another consideration when characterizing etching
performance is producing isotropic etches. Isotropic
etches, meaning etches having uniform etch properties in
25 all directions, are desirable.

Silicon micromachining in MEMS often uses wet
chemical and plasma etching. Wet chemical etching is a
purely chemical process having three steps: movement of
the etchant species to the surface of the wafer, chemical
30 reaction with the exposed film that produces soluble

- 2 -

byproducts, and movement of the reaction products away from the surface of the wafer. Wet etching often yields high selectivity. However, wet etching can have serious drawbacks such as poor process control and excessive particle contamination. Chemical etchants also can cause surface tension effects during drying. The meniscus force of the liquid etchant can drag on the free standing structure thereby sticking to the structure's surface which can induce direct mechanical damage.

Etching in a plasma environment has several advantages when compared to wet etching. Plasmas are easier to start and stop at precise times defining the beginning and end respectively of the etching process as compared with simple immersion wet etching. Plasma etch processes are much less sensitive to small changes in the temperature of the wafer. Plasma etching involves less contaminant and no damage to fragile structures due to surface tension and stiction forces of wet etchants.

Plasma etching is carried out by introducing a feed gas into the chamber. The feed gas is broken down into chemically reactive species by the plasma. These chemically reactive species diffuse to the surface of the wafer and are adsorbed. The species react with the exposed film. The reaction product is desorbed, diffused away from the wafer, and is transported by gas stream out of the etch chamber.

Plasma etch processes obviate many of the wet chemical etch problems. However, plasma etching has limited selectivity over silicon dioxide and nitride. The plasma environment also produces ions and soft x-ray radiation which can damage or have undesirable charging effects on the electronic devices on the substrate.

- 3 -

In "Plasma-less Dry Etching of Silicon with Fluorine-Containing Compounds", Lbbotson et al, J. Appl. Phys., Vol. 56(10), 1984, p. 2939-2942; it was suggested
5 that some fluorine-containing interhalogens such as xenon difluoride can etch silicon spontaneously in the vapor phase.

Summary

10 The present invention provides an apparatus and method for gas-phase bromine trifluoride (BrF_3) silicon isotropic room temperature etching system for both bulk and surface micromachining. Gas-phase BrF_3 etching has many advantages. BrF_3 has a high vapor pressure at room
15 temperature. This allows ease of use and high etching rate. Gas-phase BrF_3 etching produces fewer damaging meniscus and stiction forces and is relatively contamination-free. Gas-phase BrF_3 etching produces longer undercut distance than plasma etching and produces
20 no damage to the electronics device on the substrate.

The BrF_3 containing gas-phase etchant can be applied in a pulse mode and in a continuous flow mode. The BrF_3 gas can be diluted with another gas and this mixture can be used as the gas-phase etchant. The
25 etching rate in pulse mode is dependent on gas concentration, reaction pressure, pulse duration, pattern opening area and effective surface area.

An apparatus and method for BrF_3 containing gas-phase etching is provided.

Brief Description of the Drawing

30 These and other aspects will be described with reference to the drawings, in which:

- 4 -

- FIG. 1A shows a preferred etching apparatus;
FIG. 1B shows the steps in one etching pulse;
FIG. 2 illustrates etching rates at different BrF_3
5 pressures;
FIG. 3 illustrates silicon mass loss vs. pulse
duration time for different exposed silicon areas;
FIG. 4 illustrates vertical and horizontal etching
depth vs. Circular opening with varying diameters;
10 FIG. 5 illustrates vertical etching depth vs.
number of pulses with different circular opening sizes;
FIG. 6 shows local loading effect and aperture
opening effect;
FIG. 7 illustrates surface micromachined channels;
15 FIG. 8 illustrates surface micromachined
membranes;
FIG. 9 illustrates etching length in surface
micromachined channels vs. number of pulses; and
FIG. 10A and 10B compares the effect of BrF_3
20 dilution on surface roughness.

Description of the Preferred Embodiments

ETCHING CHEMISTRY

The literature does not suggest any efficient
methods and apparatus of using BrF_3 gas for silicon
25 micromachining. At room temperature, BrF_3 is in the form
of a colorless to gray yellow liquid with a vapor
pressure of approximately 7.0 Torr. When compared with
xenon difluoride (XeF_2), bromine trifluoride is easier to
vaporize. XeF_2 has a vapor pressure of approximately 3.0
30 Torr and exists as a white powder at room temperature.
 BrF_3 exists as a liquid at room temperature. This is
advantageous since the etchant can be stored as a liquid.
Liquids are usually easier to store in process chambers

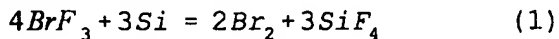
- 5 -

and to vaporize than solid powder. BrF_3 has more fluorine atoms than XeF_2 per molecule. Hence, BrF_3 has a higher etching efficiency than that of XeF_2 because fluorine
5 atoms are believed to be the active etching molecule. BrF_3 etching is also cost effective when compared with the use of XeF_2 . The cost of BrF_3 etching can be as low as 10% of the cost of XeF_2 etching.

The etching mechanism of gas-phase BrF_3 with
10 silicon is believed to be similar to that of other fluorine-containing interhalogens. The mechanism is believed to include: (1) nondissociative adsorption of gas-phase species at the surface of the solid being etched; (2) dissociation of this adsorbed gas; (3)
15 reaction between adsorbed atoms and the solid surface to form an adsorbed product molecule (SiF_4); (4) desorption of the product molecule into the gas phase. Adsorption is the adhesion of an extremely thin layer of molecules to the surfaces of solid bodies with which the molecules
20 are in contact. Desorption is the release of product molecules from a surface.

Pure BrF_3 gas can be used as a gas-phase etchant. A mixture of BrF_3 with another compound can also be used as a gas-phase etchant. One embodiment features diluting
25 BrF_3 with xenon gas to control the etching surface roughness produced.

The etching of silicon on the surface is believed to be done by fluorine atoms. The volatile products, SiF_4 and Br_2 , are produced as shown in equation (1):



30 Assuming the etching process is limited by chemical reaction and the BrF_3 concentration is uniform in the reaction chamber, the number of BrF_3 molecules in the

- 6 -

reaction chamber, N , can be expressed as equation (2),

$$-\frac{dN}{dt} = \frac{4}{3} RA \times n_{si} \quad (2)$$

where R is the silicon etching rate in angstrom/minute, n_{si} is the atomic density of silicon, and A is the silicon opening area of the etching sample.

The BrF_3 etching rate is shown as a function of silicon substrate temperature and fitted to the Arrhenius equation in the form of equation (3),

$$R = 1.16 \times 10^{-18} \frac{N}{V} T^{1/2} \text{Exp}(-E_a / kT) \quad (\text{\AA}/\text{minute}) \quad (3)$$

where E_a is the activation energy that has a value of -6.4 kcal/mole for BrF_3 at room temperature, k is the Boltzmann constant (1.987×10^{-3} kcal/mole/K). In the preferred embodiment, T is 300K, V is 2220 cm^3 , the initial value of N is 7.76×10^{19} .

At 1.0 Torr gas pressure and room temperature, equation (3) gives an etching rate of $4.13 \text{ }\mu\text{m}/\text{min}$ in the preferred system.

By combining equation (2) and equation (3) and solving the first-order differential equation, the number of BrF_3 molecules in the reaction chamber, N , is found to be an exponential function of time. N can be converted to the silicon mass loss as a function of etching time, $M(t)$ as in equation (4),

$$M(t) = M(\infty) \left[1 - \text{Exp} \left(-\frac{t}{\tau} \right) \right] \quad (4)$$

- 7 -

where τ is shown in equation (5),

$$\tau = C \frac{V}{A} \quad (\text{second}) \quad (5)$$

C is a constant and has a value of 8.78×10^{-2} s/cm for the present system. Equation (5) shows that the time
5 constant is inversely proportional to the silicon exposed area A. For the opening area of 3cm^2 , equation (5) gives a time constant of 65 seconds.

ETCHING APPARATUS AND OPERATION

Figure 1A shows the preferred etching apparatus
10 having a reaction chamber 110, a vapor reservoir 120, nitrogen purge source 130, xenon dilution system 140 and a vacuum subsystem 150. Individual gas flow is controlled by switching the corresponding valve 174, 178.

Valve 176 regulates the flow of gas from the vapor
15 reservoir 120 to the reaction chamber 110. Valve 172 regulates the flow of gas from the reaction chamber 110 to the vacuum subsystem 150. Pressure in the vapor reservoir 120 and reaction chamber 110 are monitored by a pressure sensor, e.g., baratron 160 and a pressure gauge
20 170 respectively.

The vapor reservoir 120 is used to contain certain vapors prior to introduction into reaction chamber 110. Gases are held at the vapor reservoir 120 to control dilution concentration. The vapor reservoir is coupled
25 to the reaction chamber. A 1900cc reaction chamber 110 and a 320cc vapor reservoir 120 can process approximately ten 4 inch wafers. The size of the chamber and reservoir are modified to accommodate the amount and size of the wafers to be processed.

- 8 -

In one embodiment, the reaction chamber 110, vapor reservoir 120, the interconnecting pipes, valves and any other part of the apparatus that may come in contact with BrF_3 is covered with a layer of corrosive resistant coating. Preferably, a thin layer of Parylene-C polymer film is deposited by chemical vapor deposition at room temperature. Parylene is chemically inert and prevents BrF_3 corrosion of the construction materials. The organic interior coating will give increased hydrophobicity to the apparatus thereby preventing undesirable condensation of gas onto the apparatus surfaces. Polyimide is another organic material that can be used as corrosive-resistant coating. Parylene-C is preferred because Parylene-C is easily applied to the apparatus by chemical vapor deposition at room temperature.

Nitrogen purge 130 is used to introduce nitrogen gas which removes contaminants and water from the wafer surface.

A xenon dilution system 140 is used to dilute the amount of BrF_3 used in the reaction. A preferred dilution ratio is 1 Torr of BrF_3 to 99 Torr of pure xenon gas. The inventors found that BrF_3 has a very high reaction rate which may produce uneven etches due to a diffusion limited effect. The diffusion limited effect is defined as when a reaction is limited by the time the molecules come in contact with the surface rather than the amount of reactants. Hence, some molecules may reach the surface faster than others producing an uneven etch. Dilution with xenon reduces the mean free path, as a result, BrF_3 molecules are scattered more uniformly at a higher reaction pressure thereby resulting in a smoother surface.

- 9 -

Baratron 160 is a sensitive, short range, pressure measuring device. The baratron measures a capacitance change when the pressure changes. The baratron is used in this embodiment to measure pressure changes within a 10 Torr range. The baratron is used as a vapor pressure sensor, positioned to measure a pressure of the vapor reservoir 120. The pressure gauge 170 is a wide range pressure dial which is used to measure a range from 0 to 500 Torr in this embodiment. The pressure gauge 170 is used as a reaction pressure sensor positioned to measure a pressure of the reaction chamber 110.

The construction materials are preferably stainless steel, brass, and nickel. A more costly material such as monel can also be used. Monel is more BrF_3 corrosive-resistant than stainless steel and brass. Other BrF_3 corrosive-resistant materials can also be used. The inventors found a method to improve the corrosive-resistant properties of less expensive metals, e.g. stainless steel and brass, by the application of Parylene-C polymer film. This corrosive-resistant coating enables the use of less expensive metals as construction materials by making these metals more BrF_3 corrosive-resistant.

For safety reasons, the whole apparatus system is set up inside a ventilated fume hood 180. The process can be automated in which case controller 190 can control the valves. Alternatively, the entire process can be manual.

The inventors found that the characteristics of BrF_3 gas are different than other etchants which have been used. In order to exploit these characteristics, etching processes are preferably conducted using pulse BrF_3 flow etching. Alternately, continuous flow of BrF_3 vapor can

- 10 -

also be used. The apparatus as shown in FIG. 1A can be adapted for continuous flow operation. Mass flow controls 195, 197, are positioned to regulate the
5 continuous flow rate of BrF_3 and Xe respectively during continuous flow operation.

However, such continuous flow of BrF_3 vapor will etch silicon very fast which makes the etching difficult to control. Also, continuous BrF_3 flow has a low etching
10 efficiency. Continuous flow of BrF_3 leaves a significant amount of unconsumed BrF_3 vapor; this vapor can enter the pump system and may cause safety concerns and pump corrosion.

The etching process begins by loading the wafers
15 in the reaction chamber 110. Vacuum subsystem 150 is used to evacuate both the reaction chamber 110 and vapor reservoir 120 to below 10 mTorr. The pressure of the reaction chamber 110 can be read from pressure gauge 170. The chamber separation valve 172 is then closed. Valve
20 174 is opened to inject a fixed amount of BrF_3 into the vapor reservoir 120, e.g., around 10^{-4} moles of material, depending on amount of samples to be processed. For a load of five 4 inch wafers, 7 Torr of BrF_3 are preferably used. The chamber separation valve 176 is then opened
25 to allow BrF_3 vapor to enter the reaction chamber 110. Enough time is given to make sure all the BrF_3 vapor inside the reaction chamber 110 is consumed. This reaction time is dependent on the number and size of the wafer being processed. Finally, the chamber separation
30 valve 172 is opened and both the reaction chamber 110 and vapor reservoir 120 are again pumped down. The above procedures define one pulse of the etching process. The process is continued for each pulse.

- 11 -

Figure 1B summarizes the steps in one etching pulse. In step A, valves 176 and 172 are opened and valve 174 is closed. The open valves 176 and 172 allow the vacuum subsystem 150 to evacuate the vapor reservoir 120 and the reaction chamber 110. Step B introduces the gas-phase etchant into the vapor reservoir. Valve 174 is opened to allow the gas-phase etchant to fill vapor reservoir 120. Valve 176 is closed to prevent the gas from vapor reservoir 120 to fill reaction chamber 110. In step C, valve 176 is opened to allow the gas-phase etchant from the vapor reservoir 120 to fill the reaction chamber 110. The valves 174 and 172 are closed to prevent escape of the gas-phase etchant. Step D closes valve 176 and valve 172, thereby isolating a controlled gas-phase etchant atmosphere inside the reaction chamber 110. Step D lasts for a duration sufficient for all of the gas-phase etchant to be consumed. Another pulse is applied by repeating steps B to D.

At room temperature and 6 Torr pressure in the vapor reservoir 120, the number of BrF_3 molecules in one pulse is calculated to be around 1.29×10^{-4} mole. When the atmosphere in the vapor reservoir equalizes with reaction chamber 110, there is 1.1×10^{-4} mole of BrF_3 in the reaction chamber 110. According to the equations (1) to (5), theoretically up to 2.3 mg of silicon can be etched away per pulse.

SAMPLE PREPARATION

Silicon etching processes are conducted on silicon dice with edges covered by hard baked photoresist, which is shown later to have a very low etching rate. The material is first prepared to remove the native oxide on the silicon surface. The samples are etched in buffered

- 12 -

hydrofluoric acid for 10 seconds followed by deionized water rinse and nitrogen drying before etching. This removes the native oxide on the silicon surface. This cleaning step removes the native oxide so that the BrF_3 can react with the silicon surface directly when introduced in the reaction chamber 110. Without the cleaning step, BrF_3 vapors are sufficient to remove the native oxide. Once the BrF_3 removes the native oxide then the etchant will proceed to etch the silicon surface.

Samples are then loaded into the reaction chamber 110 which is evacuated to 10 mTorr. The samples are then dried. A vacuum is applied to vaporize the moisture on the sample surface. Samples are maintained under vacuum for at least 10 minutes before starting the first BrF_3 pulse. This process time under vacuum is also dependent on the size and amount of wafers to be processed. Nitrogen gas is then applied to blow away any residual moisture and contaminants before starting the first BrF_3 pulse. Nitrogen valve 178 and chamber separation valve 176 are opened to introduce the nitrogen gas.

Nitrogen gas (N_2) drying produces reliable and repeatable etching. Baking the sample at high temperature for drying can also be done but is not necessary. Acetone cleaning is undesirable. A white polymer-like film forms on the silicon surface when acetone residue is exposed to BrF_3 vapor. This white film is undesirable because the film stops further etching.

The etching depth and the undercut can be measured, e.g. using a microscope with a calibrated focus. The thickness of the mask layers before and after the etching is determined using a Nanospec thin-film thickness measurement instrument, available from Nanometrics, Sunnyvale, CA. The roughness of the silicon

- 13 -

surface is measured using a surface profiler preferably a Tencor α -step 200(TM) available from Tencor Instruments. SEM photographs of surface roughness can be taken;
5 surface roughness are measured by scales on the SEM photograph.

ETCHING CHARACTERIZATION AND PERFORMANCE

Bulk Silicon Etching

10 A first example carries out bulk silicon etching processes on silicon chips with circular openings. Single-crystal silicon, Polysilicon, and amorphous silicon have all been etched effectively using BrF_3 containing gas-phase etchant. The diameter ranges from 4
15 m to 4 mm; other diameters can also be used. Different masking materials such as thermal oxide, LPCVD silicon nitride, hard-baked AZ4400 and AZ1518 photoresist are used as the mask materials to characterize the etching rate and etching selectivity.

20 The etching rate of one constant sample opening with variable gas pressures and constant pulse duration is measured. The samples have 800 μm circular window openings and the constant pulse duration is 10 minutes. Figure 2 shows the vertical etching depth as a function
25 of the number of pulses at different BrF_3 pressures. The etching rate ranges from 10 $\mu\text{m}/\text{pulse}$ up to 140 $\mu\text{m}/\text{pulse}$, which correspond to an average etching rate range from 1 $\mu\text{m}/\text{min}$ up to 14 $\mu\text{m}/\text{min}$ for this particular opening of 800 μm . The vertical etching depth increases as the number
30 of pulses applied increases.

The amount of sample etched under various pulse durations is measured. The BrF_3 pressure is constant at 1 Torr while the pulse duration time is varied from 20 seconds to 20 minutes. Figure 3 shows the mass of silicon

- 14 -

etched away versus pulse duration time with different window opening areas. The samples with different openings are tested separately. Figure 3 shows that not only the etching rate but also the system etching efficiency is a function of exposed silicon area. The system efficiency is defined as the ratio of the silicon mass etched by the system to the theoretical silicon mass etched assuming all the BrF_3 is consumed by silicon, which is 2.3 mg in the preferred system. The efficiency from Figure 3 is 80% for a 4 inch (160cm^2) bare silicon wafer.

The etching rate as the function of the opening area is measured. Circular openings with diameters from $4\text{ }\mu\text{m}$ to 4 mm are used. All the samples are etched in the same load. The BrF_3 pressure is 1 Torr and the pulse duration is 15 minutes. The etching depth and undercut of these samples versus the sample opening area are plotted in Figure 4.

Figure 4 shows that the etching depth of the $40\text{ }\mu\text{m}$ to $200\text{ }\mu\text{m}$ samples are about 50% more than the larger samples. For the samples with diameters under $40\text{ }\mu\text{m}$, smaller openings allow less silicon to be etched. Another series of samples are processed with the same type of samples using 500 mTorr, and 15 consecutive pulses at 1 min./pulse. All the samples are etched at the same time. The results shown in Figure 5 agrees with the results of Figure 4.

Equation (5) shows that the etching time constant τ is inversely proportional to the surface area. The bulk etching process results in Figure 3 indicate such a qualitative relationship. Since the BrF_3 etched silicon surface is quite rough, the effective silicon surface area is larger than the mask opening area A .

- 15 -

The bulk silicon etching results in Figure 4 and Figure 5 illustrate the local loading effects for large openings, e.g. openings greater than 200 μm in diameter. 5 Aperture opening effects are also shown for small openings, e.g. those under 10 μm in diameter. These two effects can be caused by the formation of a local BrF_3 depletion region.

The diffusion limited effects can be qualitatively 10 explained by comparing the circular opening radius with the mean free path L of the gas molecules. When the opening radius r is close to L , the diffusion front profile can be represented by a semi-spherical surface with radius r , shown as opening A in Figure 6, which has 15 a surface area of $2\pi r^2$. If $r \gg L$, as in the case of opening B, it has a surface area of πr^2 , which means the number of BrF_3 molecules that reaches the silicon surface per unit area without any collision with other gas molecules is half of the case A. This explains why the 20 etching depth per pulse in B is half that of A as shown in Figure 4. In the case of opening C, after etch down a depth of d , when $d > 2r$, and $r \ll L$, the opening that allows BrF_3 molecules enter is reduced compare to the case of r similar to d , thus reducing the etching rate.

25 Etching Selectivity

Checkerboard openings of 800 μm x 800 μm on a silicon wafer with several masking materials are processed to characterize the etching selectivity. The etching selectivity of silicon to other materials is 30 found to be greater than 3000 to 1 for LPCVD silicon dioxide, and 1000 to 1 for hard baked AZ 4400 and AZ1518 photoresists. The etching rate of silicon nitride depends on the quality and silicon concentration of the

- 16 -

nitride layer and results in a selectivity range of 400:1 to 800:1. In the case of most metals, like aluminum, copper, gold, and nickel, BrF_3 forms a passivated non-volatile metal fluoride layer on the metal surface and further reaction is stopped. The selectivity over these metals is greater than 1000 to 1. The selectivity of silicon to Polyimide is greater than 1000 to 1. The selectivity of silicon to Parylene-C polymer film is greater than 10^4 to 1.

Polysilicon Sacrificial Layer Etching

As shown in Figure 7 and Figure 8, surface micromachined channels and membranes with silicon nitride as the structural layer and polysilicon as the sacrificial layer are also released by this BrF_3 etching process. Figure 9 shows that no obvious etching rate difference is found among the channels with different widths. A total length of 300 μm has been etched into the channels with 10 etching pulses. Circular membranes have similar etching rates as the channels. The present invention provides an etch rate that is independent of the desired geometry of the sample.

Surface Roughing

Figures 10A and 10B compare the effect of BrF_3 dilution on surface roughness. The inventors found that the silicon surface etched by pure BrF_3 at 1 Torr pressure is rather rough with about 2 μm roughness as shown in Figure 10A. When 99 Torr of xenon (Xe) gas is added to the 1 Torr BrF_3 , the BrF_3 molecules have a much shorter mean free path and are scattered more uniformly under the higher reaction press. This effect reduces the surface roughness to about 0.1 μm as shown in Figure 10B.

- 17 -

Consistent etching results and high molecular etching efficiency (80%) have been achieved by performing the etching in a controlled pulse mode. This pure
5 gaseous BrF_3 etching process is isotropic and has a high etch rate with high selectivity over silicon dioxide (3000:1), silicon nitride (400-800:1) and photoresist (1000:1). Gaseous BrF_3 etching can also be used in surface micromachining process, where silicon nitride
10 channels and membranes using polysilicon as the sacrificial layer have been successfully fabricated. Gas-phase BrF_3 etching is simple, fast, maskable, and repeatable.

Although only a few embodiments have been
15 described in detail above, those having ordinary skill in the art will certainly understand that many modifications are possible in the preferred embodiment without departing from the teachings thereof. For example, materials other than silicon can be etched in this way.

20 All such modifications are intended to be encompassed within the following claims.

- 18 -

What is claimed is:

1. A method of etching in micromachining processes, comprising:
 - 5 obtaining a sample of a material that can be etched using bromine trifluoride;
treating said sample by contacting said sample with a gas-phase bromine trifluoride containing etchant to produce a desired etch depth in said sample.
- 10 2. A method as in claim 1, wherein said treating comprises introducing a specific amount of etchant into a chamber with said sample, leaving said etchant in said chamber for a specified time, and then introducing another specific amount of etchant in said chamber to
15 define a pulsed operation.
3. A method as in claim 2, wherein said sample is a silicon containing material.
4. A method as in claim 1, wherein said treating comprises storing said etchant as a liquid material,
20 converting the liquid to a gaseous phase, and introducing the gaseous phase material into an etching chamber.
5. A method of etching in micromachining processes, comprising:
 - 25 obtaining a sample;
treating said sample by contacting said sample with a gas-phase etchant, for a time defining a portion of a pulse train, wherein said time lasts for a specified duration;

- 19 -

at the end of said time of said specified duration, stopping contacting said sample with said gas-phase etchant;

- 5 repeating said treating for said specified duration and said stopping, to produce a desired etch depth.

6. A method as in claim 5, wherein said sample includes silicon.

- 10 7. A method as in claim 5, wherein said gas-phase etchant is bromine trifluoride (BrF_3).

8. A method as in claim 5, wherein said specified duration is when a specified amount of the gas-phase etchant is consumed.

- 15 9. A method as in claim 5, wherein said treating comprises storing said etchant as a liquid material, converting the liquid to a gaseous phase, and introducing the gaseous phase material into an etching chamber.

10. A method of etching, comprising:
20 providing a sample in a chamber;
 evacuating said chamber to a specified level of evacuation;
 introducing a fixed amount of gas-phase etchant into said environment;
25 exposing said sample to said gas-phase etchant for a specified duration;
 removing said gas-phase etchant from said environment, wherein said introducing, exposing and

- 20 -

removing forms one pulse of an etching process;
applying a specified number of additional pulses.

11. A method as in claim 10, wherein said gas-
5 phase etchant is bromine trifluoride (BrF_3).

12. A method as in claim 10, wherein said
treating comprises storing said etchant as a liquid
material, converting the liquid to a gaseous phase, and
introducing the gaseous phase material into an etching
10 chamber.

13. A method of etching a substrate, comprising:
obtaining a substrate of a material that can be
processed using semiconductor techniques;
pre-treating said substrate with a cleaning
15 solution which removes a native oxide from a surface of
said substrate;
using a solution including nitrogen to dry said
substrate;
placing said substrate in a sample processing
20 chamber;
introducing a fixed amount of gas-phase etchant at
a determined pressure into said sample processing
chamber;
exposing said sample to said gas-phase etchant for
25 a specified duration;
ending said exposing; and
after said ending, exposing said sample to another
pulse of exposing said sample for a specified duration.

14. A method as in claim 13, wherein said cleaning
30 solution is a solution of hydrofluoric acid.

- 21 -

15. A method as in claim 13, wherein said solution of hydrofluoric acid is followed by treating with deionized water.

5 16. A method as in claim 13, wherein said gas-phase etchant is bromine trifluoride (BrF_3).

17. A method as in claim 13, wherein said cleaning solution is not acetone.

10 18. An etching apparatus, comprising:
 a reaction chamber;
 a reaction pressure sensor positioned to measure a pressure of said reaction chamber;
 a vacuum subsystem positioned to evacuate said reaction chamber;
15 a vapor reservoir coupled to said reaction chamber;
 a vapor pressure sensor positioned to measure a pressure of the vapor reservoir;
 a gas-phase etchant source, including bromine
20 trifluoride containing gas, therein positioned to feed gas-phase etchant into said vapor reservoir and reaction chamber;
 an etchant controller, positioned between said etchant source and said reaction chamber, operating to
25 selectively allow said bromine trifluoride gas to enter said reaction chamber; and
 a valve positioned to regulate an inflow of gas from said gas source to said vapor reservoir and from said vapor reservoir to said reaction chamber.

30 19. An apparatus as in claim 18, further

- 22 -

comprising a sample drying gas source positioned to feed sample drying gas into said vapor reservoir.

20. An apparatus as in claim 19, wherein said
5 sample drying gas includes nitrogen.

21. An apparatus as in claim 18, further
comprising a xenon dilution system positioned to feed
xenon into said vapor reservoir.

22. An apparatus as in claim 18, wherein said
10 reaction chamber and said vapor reservoir are coated with
a corrosion resistant coating.

23. An apparatus as in claim 22, wherein said
corrosion resistant coating is an organic film, e.g.
Parylene-C polymer film.

15 24. An apparatus as in claim 18, wherein said
etchant source stores a liquid phase etchant which is
converted to a gas.

25. A method of etching in micromachining
processes, comprising:
20 obtaining a sample;
treating said sample by contacting said sample
with a gas-phase bromine trifluoride etchant to produce a
desired etch depth, wherein said gas-phase bromine
trifluoride etchant is diluted with a specified non
25 bromine containing gas at a specified ratio.

26. A method as in claim 25, wherein said
specified gas includes xenon.

- 23 -

27. A method as in claim 26, wherein said specified ratio is 1 Torr bromine trifluoride to 99 Torr xenon.

- 5 28. A method of gas-phase etching, comprising:
 obtaining a vapor reservoir and a reaction
 chamber, wherein said vapor reservoir is coupled to said
 reaction chamber;
 coupling a vacuum subsystem to said reaction
10 chamber and said vapor reservoir;
 obtaining a gas-phase etchant source, wherein said
 source is positioned to feed a gas-phase etchant to said
 vapor reservoir;
 positioning a first valve between said gas-phase
15 etchant source and said vapor reservoir;
 positioning a second valve between said vapor
 reservoir and said reaction chamber;
 positioning a third valve between said vacuum
 subsystem and said reaction chamber;
20 placing a sample inside said processing chamber;
 first closing said first valve while opening said
 second and third valve, allowing said vacuum subsystem to
 evacuate said reaction chamber and said vapor reservoir;
 second closing said second valve while opening
25 said first valve, allowing said gas-phase etchant to
 enter said vapor reservoir and preventing said gas-phase
 etchant to enter said reaction chamber;
 third closing said first valve and closing said
 third valve while opening said second valve, allowing
30 said gas-phase etchant to enter said reaction chamber
 from said vapor reservoir;

- 24 -

fourth closing said second and said third valve,
isolating said gas-phase etchant within said reaction
chamber for a specified duration;

5 repeating said second, third, and fourth closing
in sequence, producing a desired etch depth.

29. A method as in claim 28, wherein said
specified duration is when a specified amount of the gas-
phase etchant is consumed.

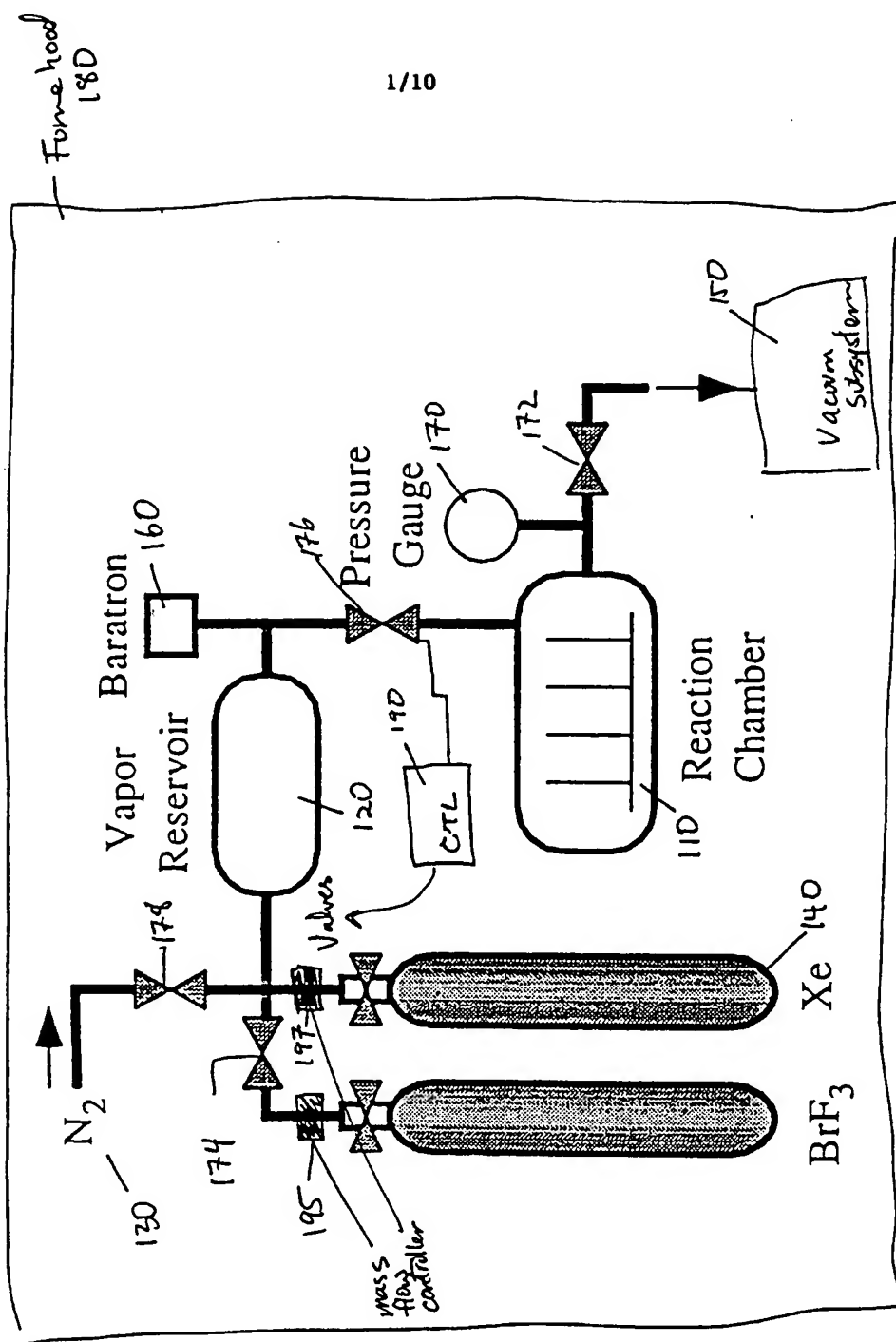


Figure 1A : Schematic of the Etching System

Operation

Definition of One Etching Pulse

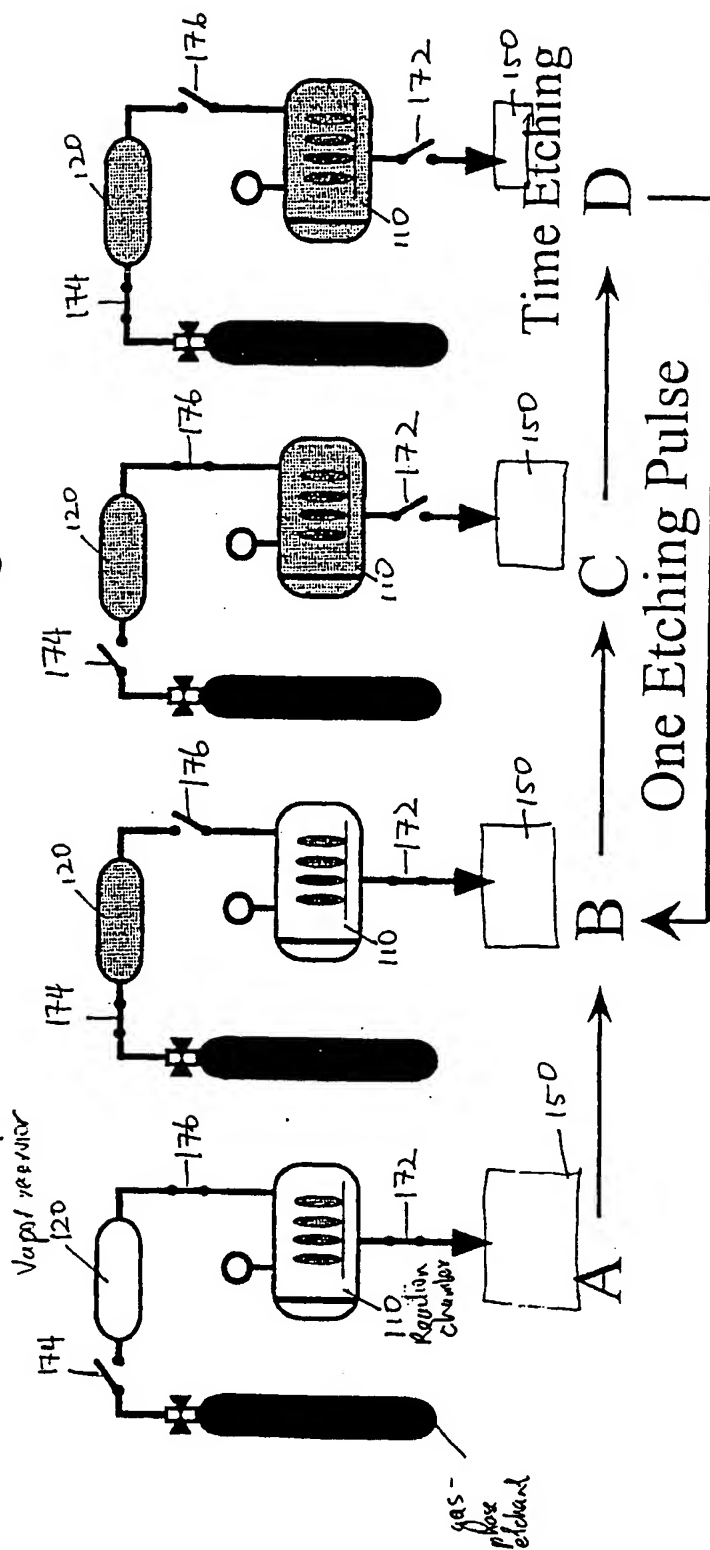


Fig.1B

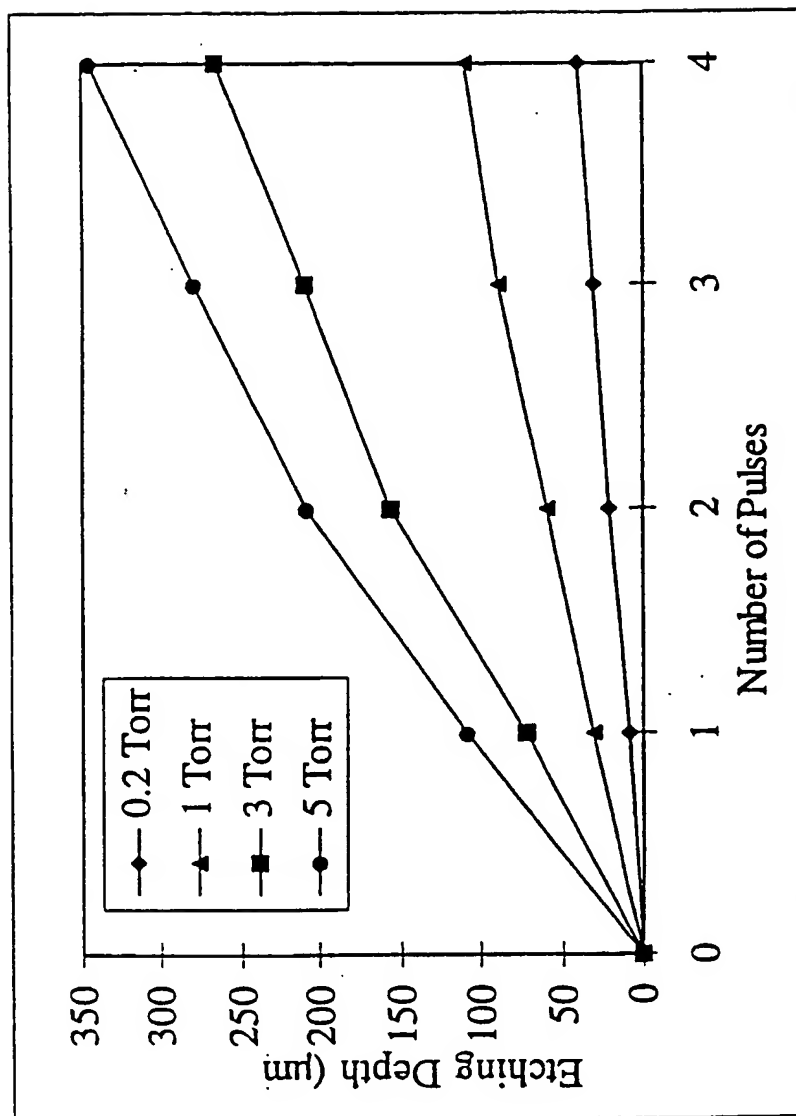


Figure 2: Etching Rates at Different BrF_3 Pressure

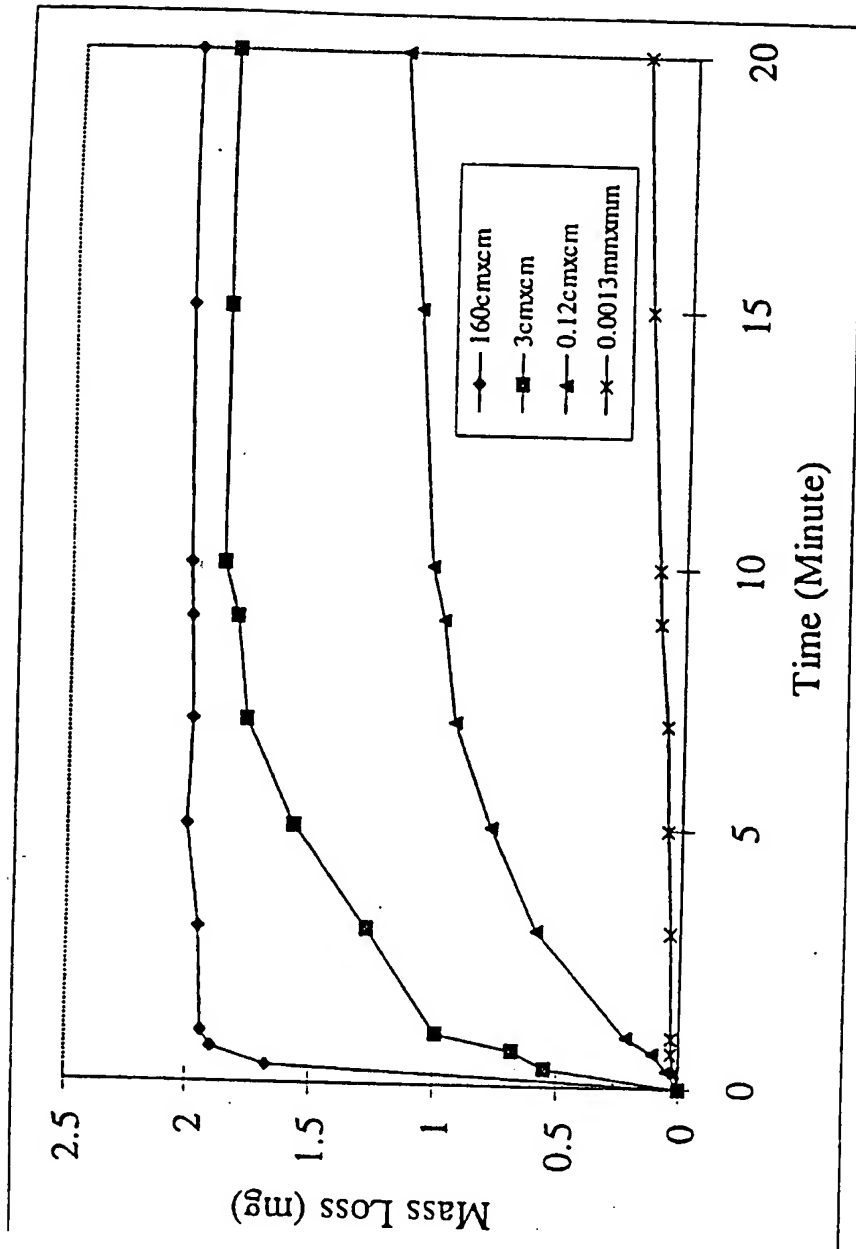


Figure 3 : Silicon Mass Loss vs. Pulse Duration Time for
Different Exposed Silicon Areas

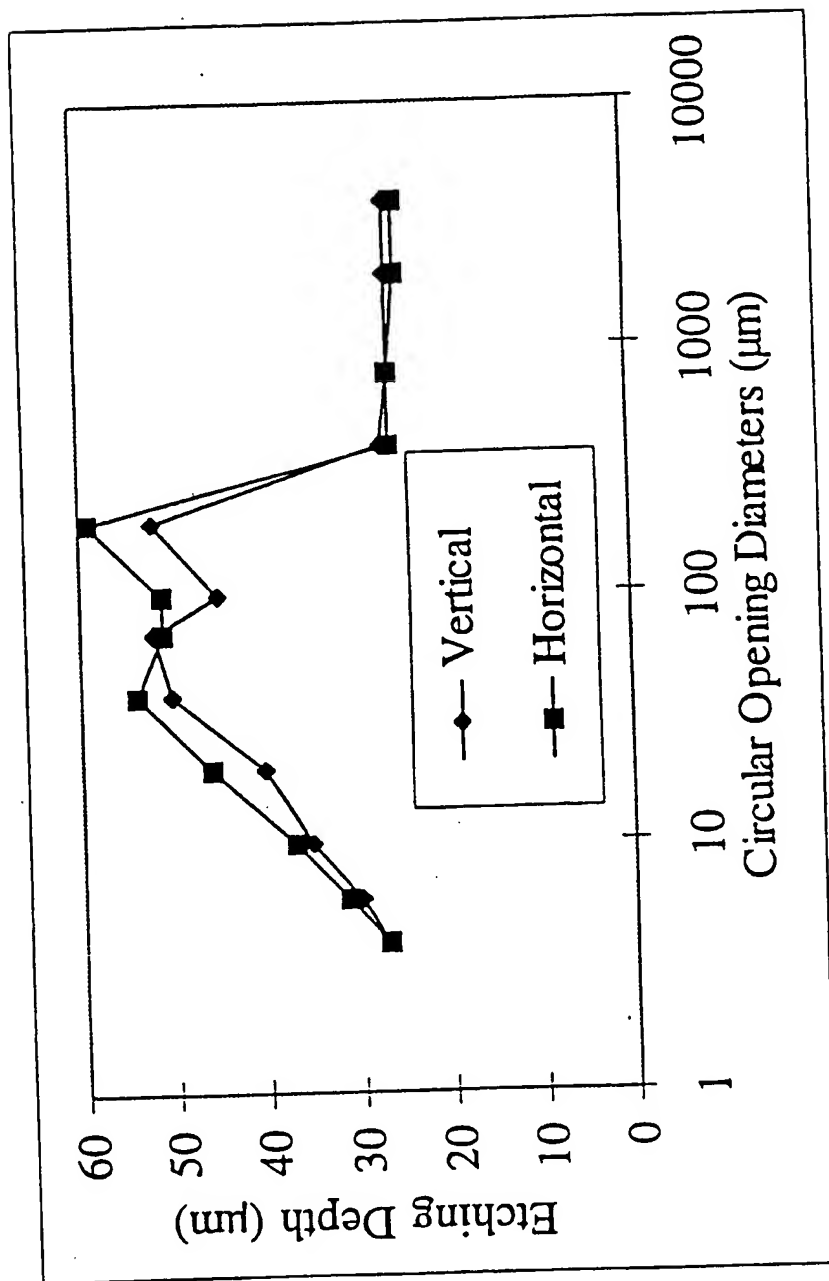


Figure 4: Vertical and Horizontal Etching Depth vs. Circular Opening with Diameters of 4μm, 8μm, 10μm, 20μm, 40μm, 70μm, 100μm, 200μm, 400μm, 800μm, 2mm, and 4mm.

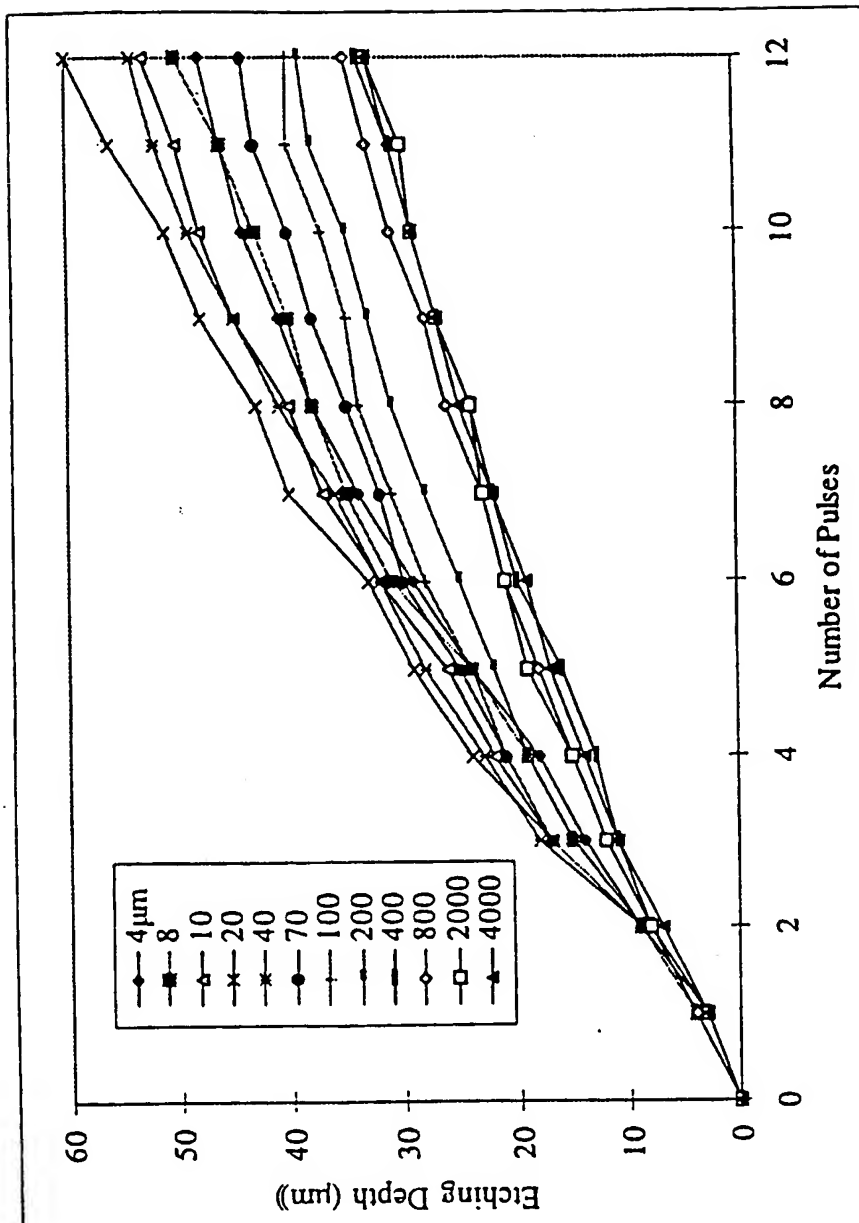


Figure 5: Vertical Etching Depth vs. Number of Pulses with
Different Circular Opening Sizes

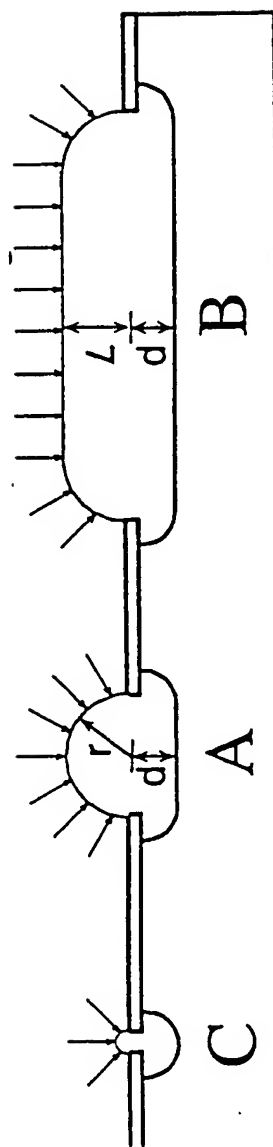


Figure 6 : Local Loading Effect and Aperture Opening Effect

8/10

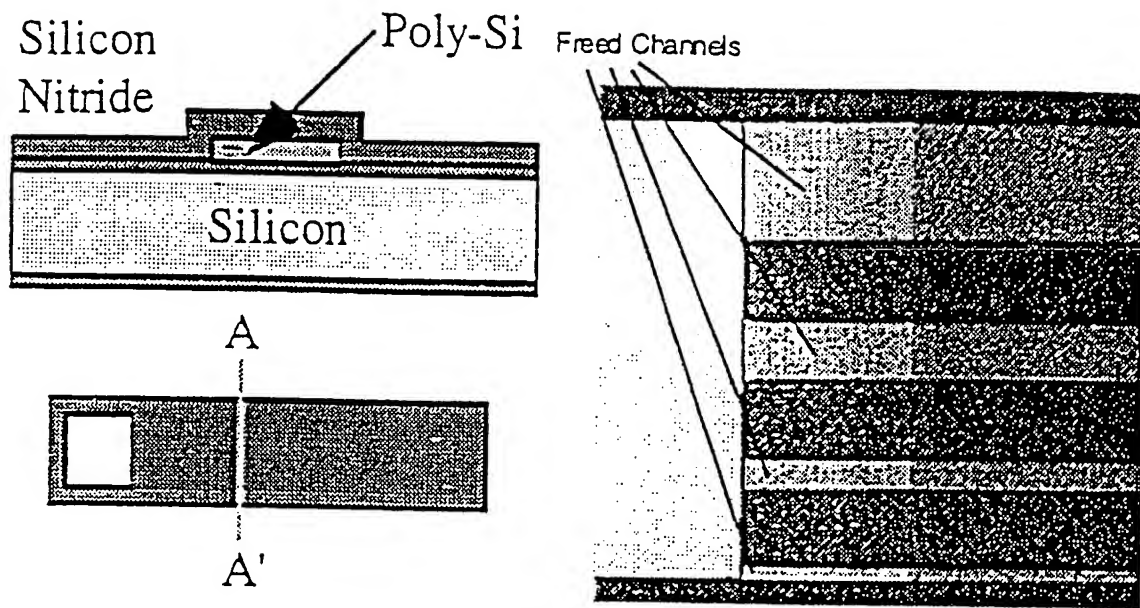


Figure 7: Surface Micromachined Channels

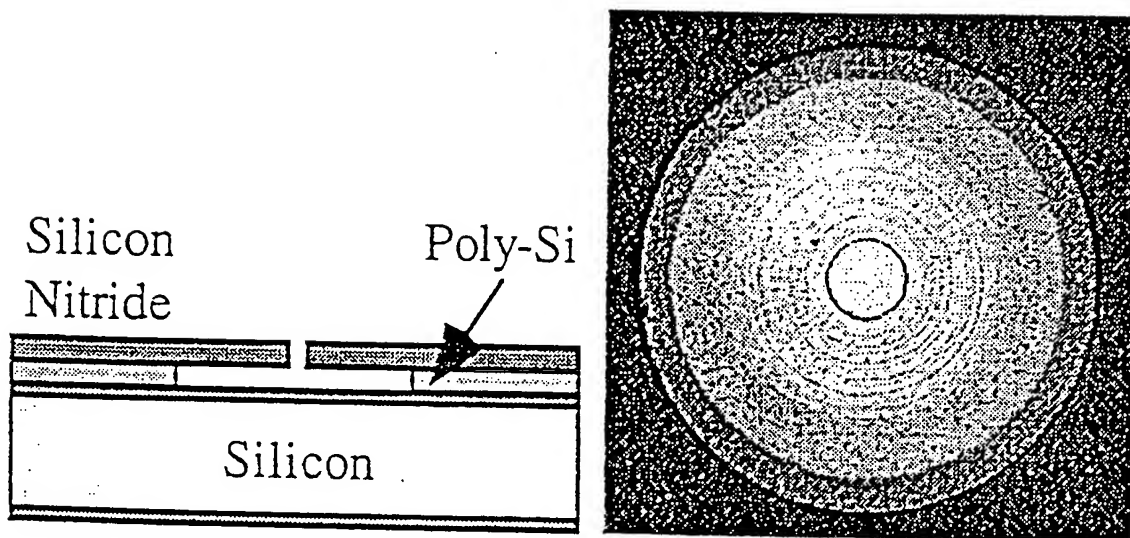
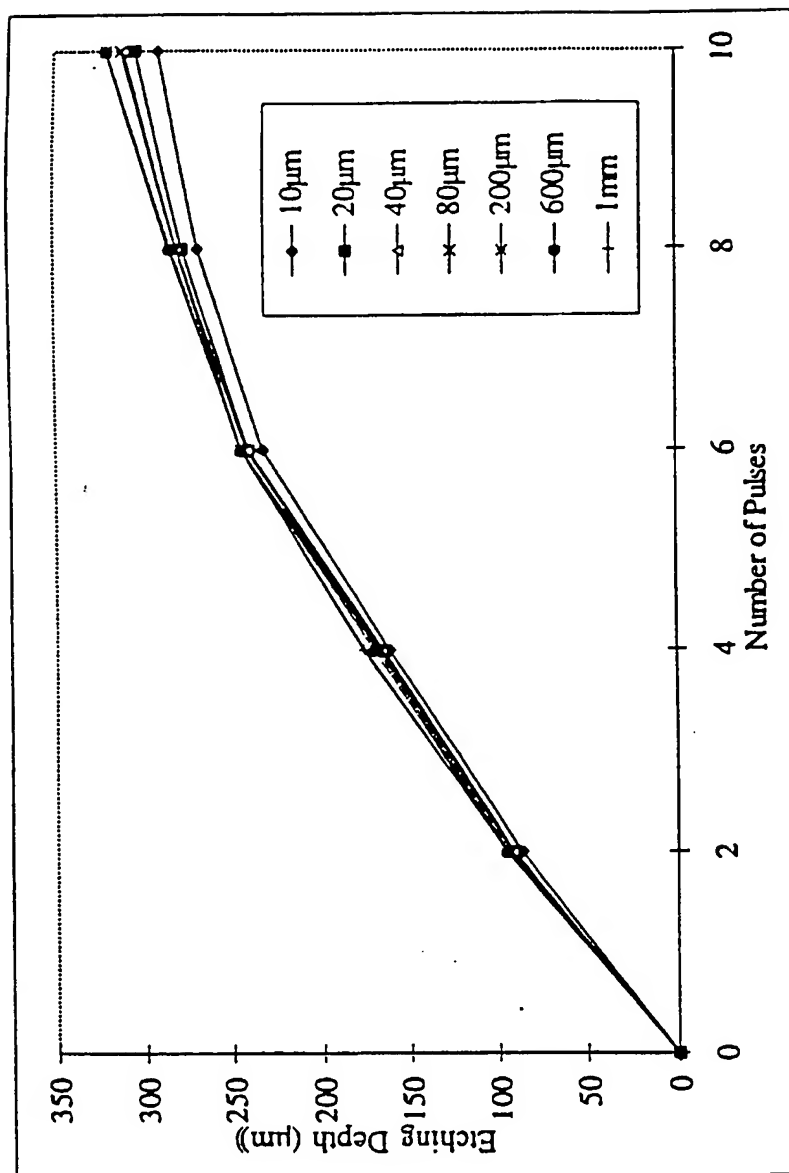
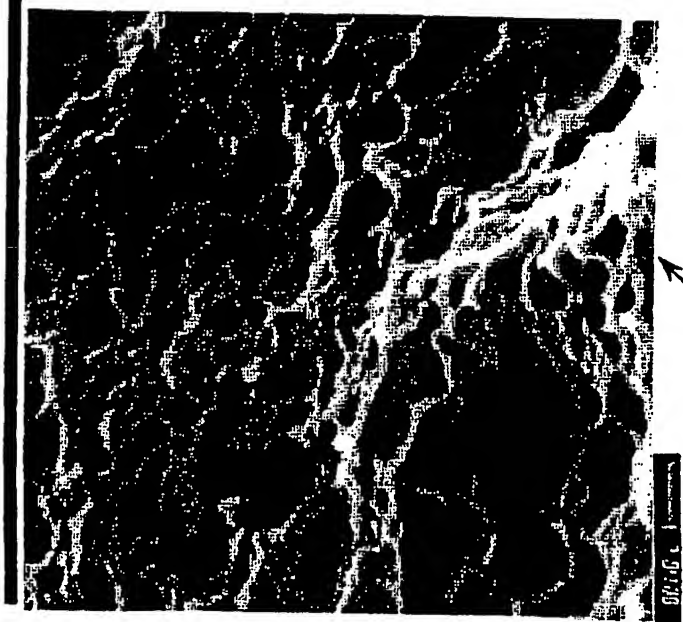


Figure 8: Surface Micromachined Membranes



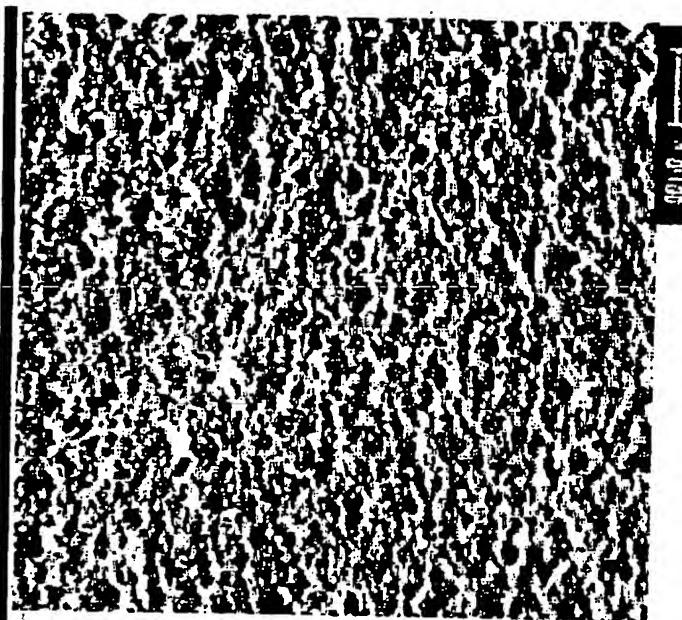
*Figure 9: Etching Length in surface Micromachined Channels
vs. Number of Pulses*

Surface Roughness



1 Torr
No Dilution

Fig. 10A



1 Torr BrF_3
+
99 Torr Xe
Fig. 10B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/01296

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01L 21/302

US CL : 216/2,49,51,57,64,67,79;438/719,964;156/345

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 216/2,49,51,57,64,67,79;438/719,964;156/345

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
APSElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IBBOTSON, D.E. et al. Plasmaless dry etching of silicon with fluorine-containing compounds. J. Appl. Phys. 15 November 1984. Vol.56. No.10. pages 2939-2942, sections II, III.B.2.	1
Y		2-17
X	US 4,498,953 A (COOK ET AL) 12 February 1985 (12-02-85), column 3, lines 17-26, column 4, example 4.	1
Y		25-27
Y	US 4,310,380 A (FLAMM ET AL) 12 January 1982 (12-01-82), column 7, lines 32-38	25-27
Y	US 4,749,440 A (BLACKWOOD ET AL) 07 June 1988 (07-06-88), Figure 1, column 6, line 55, column 7, lines 23-33, column 8, lines 15-19	18-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 APRIL 1998

Date of mailing of the international search report

30 APR 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ANITA ALANKO

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/01296

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,695,700 A (PROVENCE ET AL) 22 September 1987 (22-09-87), Figure 8.	18-23, 28-29
Y	EP 704,884 A2 (FSI INTERNATIONAL) 03 April 1996 (03-04-96), page 2, lines 46-52.	2-17,28-29

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)